

IDENTIFICATION OF FINE PARTICLE SOURCES IN MID-ATLANTIC US AREA

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Abstract. The U.S. Environmental Protection Agency (EPA) designated 20 urban areas including major cities located in mid-Atlantic US area as being in non-attainment of the new national ambient air quality standards for PM_{2.5} (particulate matter $\leq 2.5 \mu\text{m}$ in aerodynamic diameter). To support the development of effective State Implementation Plans for PM_{2.5} in the non-attainment area, 24-h integrated Speciation Trends Networks data collected in the mid-Atlantic US urban area were analyzed through the application of the positive matrix factorization (PMF).

A total of 117 to 235 samples and 27 to 29 chemical species collected at the four monitoring sites between 2001 and 2003 were analyzed and six to nine sources were identified. Secondary particles provided the highest contributions to PM_{2.5} mass concentrations (38–50% for secondary sulfate; 9–18% for secondary nitrate). Potential source contribution function analyses show the potential source areas and pathways of secondary particles contributing to this region, especially the regional influences of the biogenic as well as anthropogenic secondary particles. Motor vehicle emissions contributed 21–33% to the PM_{2.5} mass concentration. In four sites in southern New Jersey and Delaware, gasoline vehicle and diesel emissions were tentatively separated by different abundances of organic and elemental carbons. The compositional profiles for gasoline vehicle and diesel emissions are similar across this area. In addition, other combustion sources, aged sea salt, and intercontinental dust storms were identified.

Keywords: PM_{2.5}, positive matrix factorization, speciation trends network, source apportionment

1. Introduction

The association between exposure to the ambient particulate matter (PM) and adverse health effects has been shown in many studies (Dockery *et al.*, 1993; Pope *et al.*, 1995; Schwartz *et al.*, 1996). The U.S. Environmental Protection Agency (EPA) promulgated new national ambient air quality standards (NAAQS) for airborne PM (Federal Register, 1997), and established Speciation Trends Networks (STN) to characterize PM_{2.5} (particulate matter $\leq 2.5 \mu\text{m}$ in aerodynamic diameter) composition in urban areas. On December 17, 2004, U.S. EPA designated 20 urban areas (70 counties) including major cities located along the northeastern urban corridor between Washington, DC and New York city as being in non-attainment of the new NAAQS for PM_{2.5}.

Source apportionment of STN PM_{2.5} measurements are needed for developing effective State Implementation Plans (SIP) for PM_{2.5} as well as for the source-specific community epidemiology to relate adverse health effects to apportioned source contributions. Especially, the separation of regionally transported and locally originated PM_{2.5} is important in the non-attainment area. Positive matrix factorization (PMF; Paatero, 1997) has been used successfully to apportion PM_{2.5} sources in several Interagency Monitoring of Protected Visual Environments (IMPROVE; Malm *et al.*, 1994) monitoring sites (Polissar *et al.*, 1998; Song *et al.*, 2001; Maykut *et al.*, 2003; Kim and Hopke, 2004a,b). The objectives of this study are to identify PM_{2.5} sources, especially local and regional sources and estimate their contributions to PM_{2.5} mass concentrations by analysis of the data measured at the four EPA STN sites in the mid-Atlantic US urban area.

2. Experimental

2.1. SAMPLE COLLECTION AND CHEMICAL ANALYSIS

Integrated 24-h PM_{2.5} samples were collected by a Spiral Aerosol Speciation Samplers (Met One Instruments, Grants Pass, OR) on a one-in-three day schedule at the STN monitoring sites located in New Brunswick and Camden, New Jersey and a one-in-six day schedule at the monitoring sites in Wilmington and Dover, Delaware.

The monitoring locations are shown in Figure 1. The New Brunswick monitoring site is located about 40 km southwest of New York City and 60 km northeast of Philadelphia, PA. Interstate highway I-95 is situated 1 km east of the monitoring site. The monitoring site in Camden is located south of Philadelphia, PA. Interstate highway I-676 is situated 2 km west of the monitoring site. The monitoring site in Wilmington is located about 1 km southwest of downtown, 250 m southeast of the bus depot, 3 km northwest of the Port of Wilmington. Interstate highway I-95 is situated 400 m west of the site and railroad is situated within 10 m south of the site. The Dover monitoring site is located west of state highways SR 1 and Route 13/113. Railroads are situated about 2 km west of the site.

PM_{2.5} samples were collected on Teflon, Nylon, and quartz filters. The Teflon filter was used for mass concentrations and analyzed via any of five different energy dispersive X-ray fluorescence (XRF) spectrometers for the elemental analysis located in three laboratories: Chester LabNet, Cooper Environmental Services, and Research Triangle Institute (RTI). The Nylon filter is analyzed for sulfate (SO₄²⁻), nitrate (NO₃⁻), ammonium (NH₄⁺), sodium (Na⁺), and potassium (K⁺) via ion chromatography (IC). To minimize the sampling artifacts for NO₃⁻, a MgO or sodium carbonate denuder is included at the upstream of the Nylon filter (Koutrakis *et al.*, 1988; Hering *et al.*, 1999). Two instruments for anions and three instruments for cations in RTI were used for the Nylon filter analyses. The quartz filter was

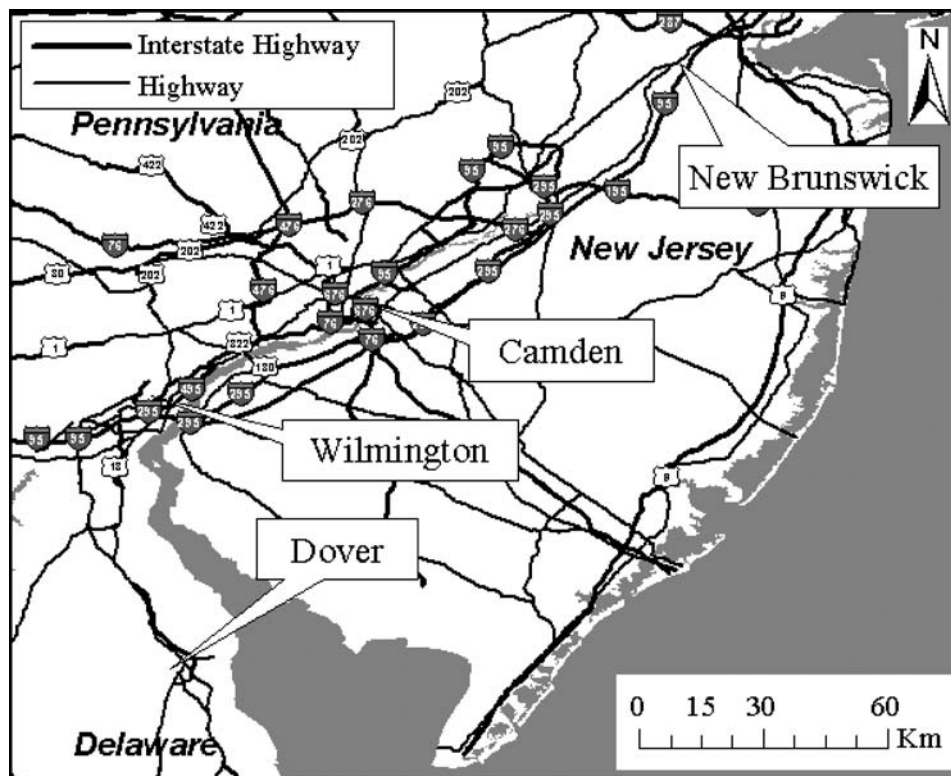


Figure 1. Location of the four Speciation Trends Network monitoring sites in New Jersey and Delaware.

analyzed by one of three instruments at RTI via National Institute for Occupational Safety and Health/Thermal Optical Transmittance (NIOSH/TOT) protocol (Birch *et al.*, 1996) for organic carbon (OC) and elemental carbon (EC).

Carbon denuders that minimize positive sampling artifact caused by adsorption of gaseous organic materials (Gundel *et al.* 1995; Pankow *et al.*, 2001) are not included upstream of the quartz filter in the STN samplers. Since the reported particulate OC concentrations were not blank corrected (RTI, 2004) and there appears to be a positive artifact in the OC concentrations measured by STN samplers, an approach suggested by Tolocka *et al.* (2001) to obtain an integrated estimate of the OC blank concentrations including trip and field blank as well as OC positive artifact on quartz filter utilizing the intercept of the regression of OC concentrations against $PM_{2.5}$ was used. The estimated OC blank values were $1.49 \mu\text{g}/\text{m}^3$ at New Brunswick, $1.65 \mu\text{g}/\text{m}^3$ at Camden, $2.69 \mu\text{g}/\text{m}^3$ at Wilmington, and $1.83 \mu\text{g}/\text{m}^3$ at Dover.

In STN data, various instruments were used to analyze samples and they produce different analytical uncertainties. Since prior to July 2003 the STN data were not

accompanied by uncertainties, a comprehensive set of error structures estimated by Kim *et al.* (2005) was used in this study.

2.2. MULTIVARIATE RECEPTOR MODELING

The receptor modeling problem can be expressed in terms of the contribution from p independent sources to all chemical species in a given sample as follows (Miller *et al.*, 1972; Hopke, 1985)

$$x_{ij} = \sum_{s=1}^p g_{is} f_{sj} + e_{ij} \quad (1)$$

where g_{is} is the particulate mass concentration from the s th source contributing to the i th sample, f_{sj} is the j th species mass fraction from the s th source, e_{ij} is residual associated with the j th species concentration measured in the i th sample, and p is the total number of independent sources. PMF provides a solution that minimizes an object function, $Q(E)$, based upon uncertainties for each observation (Paatero, 1997; Polissar *et al.*, 1998).

$$Q(E) = \left[\frac{x_{ij} - \sum_{s=1}^p g_{is} f_{sj}}{u_{ij}} \right]^2 \quad (2)$$

where u_{ij} is an uncertainty estimate in the j th constituent measured in the i th sample.

There are an infinite number of possible combinations of source contribution and profile matrices to the multivariate receptor modeling problem due to the free rotation of matrices (Henry, 1987). PMF uses non-negativity constraints on the factors to decrease rotational ambiguity. Also, the parameter FPEAK and the matrix FKEY are used to control the rotations (Lee *et al.*, 1999; Paatero *et al.*, 2002). By setting a non-zero values of FPEAK, the routine is forced to add one source contribution vector to another and subtract the corresponding source profile factors from each other and thereby yield different solutions. PMF was run with different FPEAK values to determine the range within which the object function, $Q(E)$, remains relatively constant (Paatero *et al.*, 2002; Kim *et al.*, 2003). The optimal solution should lie in this FPEAK range. In this way, subjective bias was reduced to a large extent. External information can be imposed on the solution to control the rotation. If specific species in the source profiles are known to be zero, then it is possible to pull down those values towards lower concentration through appropriate settings of FKEY resulting in the most interpretable source profiles. Each element of the FKEY matrix controls the pulling-down of the corresponding element in the

source profile matrix by setting a non-zero integer values in FKEY matrix (Lee *et al.*, 1999).

Based on the studies of Polissar *et al.* (1998), the measured concentrations below the method detection limit (MDL) values were replaced by half of the MDL values and their uncertainties were set at 5/6 of the MDL values. Missing concentrations were replaced by the geometric mean of the concentrations and their accompanying uncertainties were set at four times of this geometric mean concentration.

For the application of PMF to STN data, samples for which PM_{2.5} or OC mass concentration was not available or for which PM_{2.5} or OC mass concentration had an error flag were excluded from data sets. Samples in which blank corrected OC concentration was below zero were also excluded in this study. To obtain reasonable model fit, the sample on July 7, 2002 affected by a Canadian wildfire in which PM_{2.5} and OC mass concentrations were unusually high (e.g. 7 times and 12 times geometric mean, respectively, at New Brunswick) was excluded from the source apportionment study. Overall, 19, 38, 21, and 18% of the original data was excluded from New Brunswick, Camden, Wilmington, and Dover data, respectively. XRF S and IC SO₄²⁻ showed excellent correlations (slope = 3.2, $r^2 = 0.93$ for New Brunswick data; slope = 3.2, $r^2 = 0.98$ for Camden data; slope = 3.4, $r^2 = 0.98$ for Wilmington data; slope = 3.2, $r^2 = 0.96$ for Dover data), so it is reasonable to exclude XRF S from the analysis to prevent double counting of mass concentrations. Also, IC Na⁺ and IC K⁺ were chosen due to the higher analytical precision compared to XRF Na and XRF K. Chemical species that have values more than 90% below MDL were excluded. Thus, a total of 235 samples and 28 species, 146 samples and 29 species, 117 samples and 29 species, and 122 samples and 30 species including PM_{2.5} mass concentrations collected between June 2001 and November 2003 were used for the New Brunswick, Camden, Wilmington, and Dover analyses, respectively.

Species that have Signal/Noise (S/N) ratios between 0.2 and 2 were considered weak variables and their estimated uncertainties were increased by a factor of five to reduce their weight in the solution as recommended by Paatero and Hopke (2003). The estimated uncertainties of samples that have error flags including contaminated Na⁺ between October 2001 and January 2002 (RTI, 2004b) were increased by a factor of thirty. Summaries of PM_{2.5} speciation data are provided in Table I.

In this study, the measured PM_{2.5} mass concentration was included as an independent variable in the PMF modeling to directly obtain the mass apportionment without the usual multiple regression. The utilization of PM_{2.5} mass concentration as a variable is specified in detail in Kim *et al.* (2003).

Finally, to obtain a physically reasonable PMF solution, it was necessary to test different numbers of sources, different FPEAK values, and different FKEY matrices with the final choice based on the evaluation of the resulting source profiles as well as the quality of the species fits. The global optimum of the PMF solutions were tested by using multiple random starts for the initial values used in the iterative fitting process.

TABLE I
Summary of PM_{2.5} species mass concentrations

	New Brunswick		Camden		Wilmington		Dover	
	Arithmetic mean (ng/m ³)	Missing values (%)	Arithmetic mean (ng/m ³)	Missing values (%)	Arithmetic mean (ng/m ³)	Missing values (%)	Arithmetic mean (ng/m ³)	Missing values (%)
PM _{2.5}	14632.8	0	16922.6	0	18539.3	0	15235.2	0
OC	2515.1	2	2826.9	3	2171.4	5	1983.5	5
EC	628.2	5	680.0	3	821.5	0	467.8	11
S	1426.5	0	1729.6	0	1819.4	0	1599.3	0
NH ₄	1746.5	0	2343.5	0	2544.0	0	1960.9	0
NO ₃	1600.8	0	2273.4	0	2575.0	0	1812.2	0
Al	27.2	77	29.0	68	22.8	74	19.6	79
Au	2.5	95	3.0	89				
Ba	33.0	68	31.1	64	36.6	66	34.9	62
Br	3.2	33	5.0	27	3.9	21	3.2	28
Ca	29.7	1	34.3	1	35.5	0	33.7	3
Ce							28.1	88
Cl	33.5	75	22.0	69	35.1	62	23.7	75
Cr	2.2	73	1.7	71	1.8	63	1.5	83
Cu	5.9	27	4.3	40	13.2	3	3.1	61
Fe	74.3	0	71.3	0	112.3	0	47.7	0
K	75.2	65	94.5	68	74.8	70	64.2	70
La							20.6	89
Mg					26.9	89		
Mn	3.6	50	2.6	52	3.5	43	2.0	62
Na	210.9	8	220.9	10	225.7	6	262.0	7
Ni	3.1	43	4.1	23	4.2	13	2.2	45
P					6.6	89		
Pb	7.0	56	4.9	57	5.6	63	3.5	79
Sc	1.3	89	1.0	90			0.9	87
Se	1.7	86	2.2	70	2.1	71	1.9	75
Si	80.4	3	85.1	1	78.2	1	82.3	2
Sn			13.4	75	11.9	83	12.3	81
Sr	1.5	88	1.8	83	1.7	89	1.7	88
Ta	15.0	71	13.2	78	14.5	77	12.0	81
Ti	5.6	34	5.7	34	6.4	30	4.9	48
V	3.1	59	6.6	38	7.8	13	3.3	43
Zn	15.8	13	10.7	8	12.8	4	6.8	22

2.3. CONDITIONAL PROBABILITY FUNCTION

The conditional probability function (CPF, Kim *et al.*, 2003) analyzes local source impacts from varying wind directions using the source contribution estimates from PMF coupled with the time resolved wind directions. The CPF estimates the probability that a given source contribution from a given wind direction will exceed a predetermined threshold criterion. CPF is defined as

$$\text{CPF} = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \quad (3)$$

where $m_{\Delta\theta}$ is the number of occurrences from wind sector $\Delta\theta$ that exceeded the threshold criterion, and $n_{\Delta\theta}$ is the total number of data from the same wind sector. In this study, 24 sectors were used ($\Delta\theta = 15$ degrees). Calm winds (<1 m/s) were excluded from this analysis due to the isotropic behavior of wind vane under calm winds. From tests with several values of percentiles of the contribution from each source, a threshold criterion of the upper 25% was chosen to show the directionality of the sources. The sources are likely to be located to the direction that have high conditional probability values.

2.4. POTENTIAL SOURCE CONTRIBUTION FUNCTION

The potential source contribution function (PSCF, Ashbaugh *et al.*, 1985; Hopke *et al.*, 1995) analyzes regional source impacts. PSCF is calculated using the source contributions estimated from PMF and backward trajectories calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model and gridded meteorological data (NCEP/NCAR Reanalysis) to identify the likely locations of the secondary particles (Draxler *et al.*, 2003; Rolph, 2003). If a trajectory end point of the air parcel lies in a grid cell in an array of cells surrounding the receptor site, the trajectory is assumed to collect $\text{PM}_{2.5}$ emitted in the cell. Once the $\text{PM}_{2.5}$ is incorporated into the air parcel, it is assumed to be transported along the trajectory to the monitoring site. PSCF_{ij} is the conditional probability that an air parcel that passed through the ij th cell had a high concentration upon arrival at the monitoring site defined as

$$\text{PSCF}_{ij} = \frac{m_{ij}}{n_{ij}} \quad (4)$$

where n_{ij} is the total number of end points that fall in the ij th cell and m_{ij} is the number of end points in the same cell that are associated with samples that exceeded the threshold criterion. In this study, the average contribution of each source was used for the threshold criterion. Five-day backward trajectories starting at 12:00 at height of 500 m above the ground level were computed using the vertical mixing model every day producing 120 hourly trajectory end points per sample.

TABLE II
Average source contributions ($\mu\text{g}/\text{m}^3$) to $\text{PM}_{2.5}$ mas concentrations

Sources	Average source contribution (standard error)			
	New Brunswick	Camden	Wilmington	Dover
Secondary sulfate	6.71 (0.46)	7.23 (0.67)	6.97 (0.72)	7.50 (1.45)
Secondary nitrate	1.25 (0.10)	2.95 (0.26)	3.12 (0.28)	1.50 (0.30)
Gasoline vehicle	3.04 (0.15)	2.54 (0.16)	2.18 (0.17)	2.38 (0.35)
Diesel emissions	0.98 (0.05)	1.04 (0.06)	0.57 (0.06)	1.19 (0.20)
Local motor vehicle	0.73 (0.06)			
Bus depot			0.79 (0.09)	
Railroad			1.10 (0.08)	
Airborne soil	0.74 (0.05)	0.78 (0.09)	1.09 (0.11)	1.11 (0.21)
Aged sea salt	0.67 (0.06)	1.38(0.12)	1.03 (0.11)	1.44 (0.27)
Oil combustion		0.79 (0.08)	1.52(0.11)	
Incineration	0.19 (0.02)			

The geophysical region covered by the trajectories was divided into $1^\circ \times 1^\circ$ latitude and longitude grid cells. The sources are likely to be located in the area that have high PSCF values.

To minimize the effect of small values of n_{ij} that result in high PSCF values with a high uncertainties, an arbitrary weight function $W(n_{ij})$ was applied to down-weight the PSCF values for the cell in which the total number of end points was less than three times the average number of the end points per cell (Hopke *et al.*, 1995; Polissar *et al.*, 2001).

$$W(n_{ij}) = \begin{cases} 1.0 & 8 < n_{ij} \\ 0.7 & 3 < n_{ij} \leq 8 \\ 0.4 & 2 < n_{ij} \leq 3 \\ 0.2 & n_{ij} \leq 2 \end{cases} \quad (5)$$

3. Results and Discussion

Eight, seven, and nine-source models with values of $\text{FPEAK} = 0$ provided the most physically reasonable source profiles for the New Brunswick, Camden, and Wilmington data. For the Dover data, a six-source model with a value of $\text{FPEAK} = 0$, and a FKEY matrix provided the most reasonable source profiles. For the FKEY matrix, values of all elements were set to zero, except for a value of 5 for NH_4^+ in airborne soil. The average source contributions of each source to the $\text{PM}_{2.5}$ mass concentrations are provided in Table II.

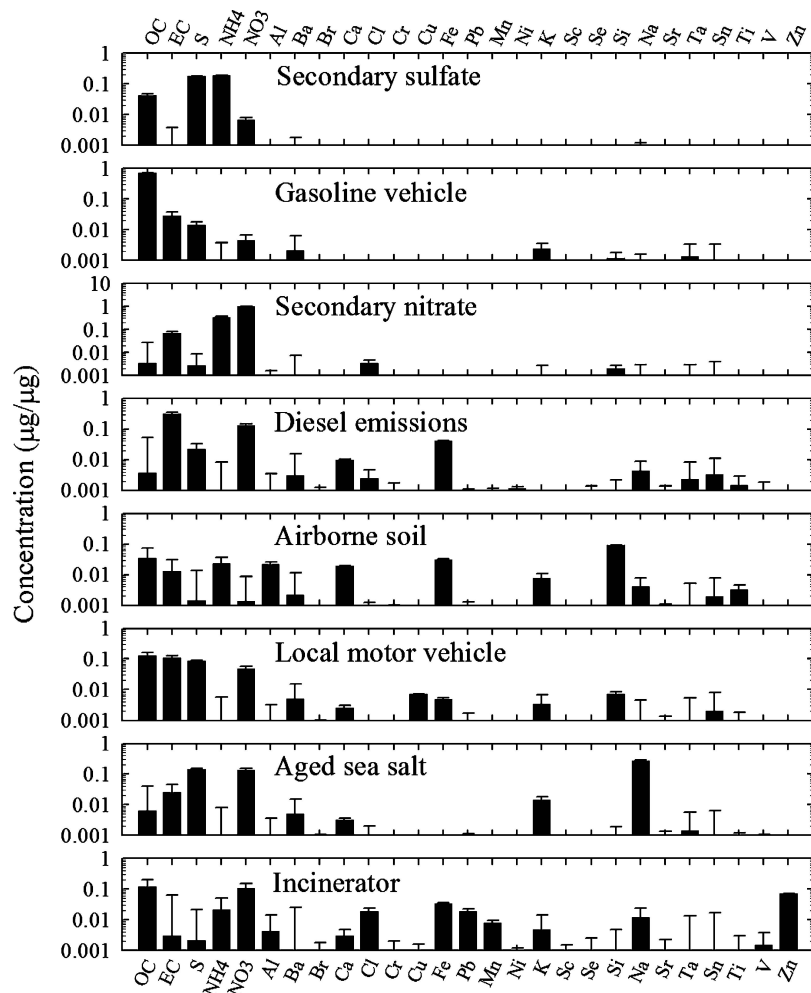


Figure 2. Source profiles deduced from PM_{2.5} samples measured at the New Brunswick site (prediction \pm standard deviation).

Comparisons of the daily reconstructed PM_{2.5} mass contributions (sum of the contributions from PMF resolved sources) with measured PM_{2.5} mass concentrations shows that the resolved sources effectively reproduce the measured values and account for most of the variation in the PM_{2.5} mass concentrations (slope = 0.93 ± 0.02 and $r^2 = 0.92$ for New Brunswick; slope = 0.97 ± 0.02 and $r^2 = 0.95$ for Camden; slope = 0.96 ± 0.02 and $r^2 = 0.95$ for Wilmington; slope = 1.04 ± 0.02 and $r^2 = 0.94$ for Dover). The PMF deduced source profiles are presented in Figures 2–5. The corresponding source contributions, CPF plots, and weekday/weekend variations are presented in the Appendix.

Secondary sulfate had the highest contribution to PM_{2.5} mass concentrations

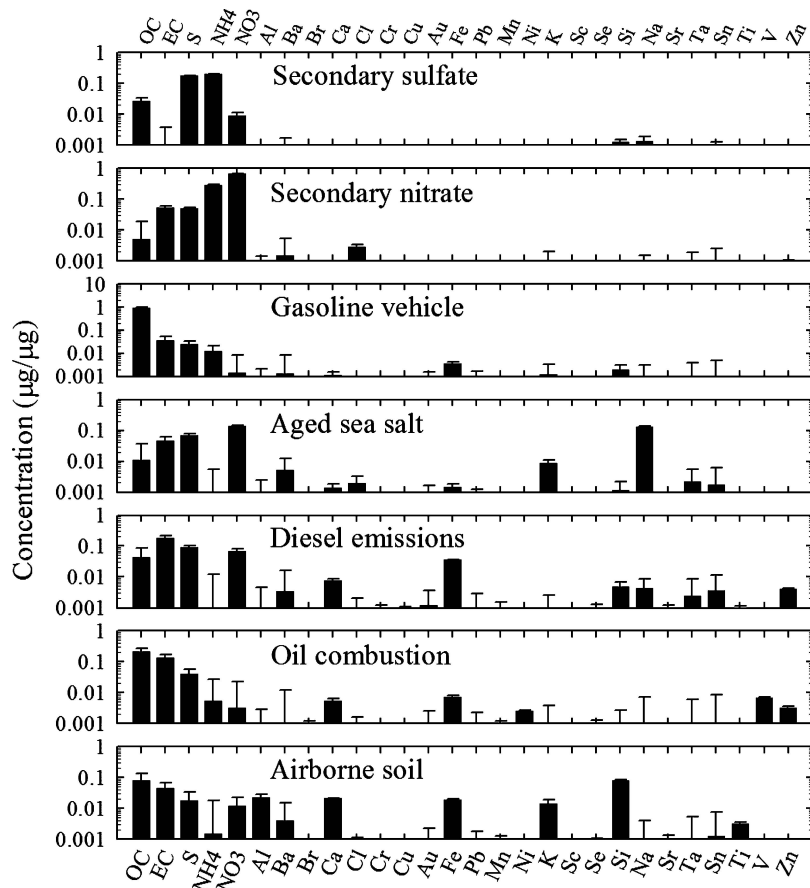


Figure 3. Source profiles deduced from $PM_{2.5}$ samples measured at the Camden site (prediction \pm standard deviation).

accounting for 38–50% of the $PM_{2.5}$ mass concentration at all four monitoring sites. Secondary sulfate is represented by its high concentrations of SO_4^{2-} and NH_4^+ . Secondary sulfate profiles typically include carbons that becomes associated with the secondary sulfate (Liu *et al.*, 2003) and this association is consistent with previous Interagency Monitoring of Protected Visual Environments (IMPROVE) studies that observed similar profiles (Kim and Hopke, 2004a,b). As shown in Figures 1, 4, 7 and 10 in the Appendix, the secondary sulfate show strong seasonal variation with higher concentrations in summer when the photochemical activity is highest.

The four monitoring sites were impacted by high concentrations of secondary sulfates: $34.1 \mu\text{g}/\text{m}^3$ (New Brunswick), $51.9 \mu\text{g}/\text{m}^3$ (Camden), $48.5 \mu\text{g}/\text{m}^3$ (Wilmington), and $43.9 \mu\text{g}/\text{m}^3$ (Dover) on July 19, 2002; $37.7 \mu\text{g}/\text{m}^3$ (New Brunswick),

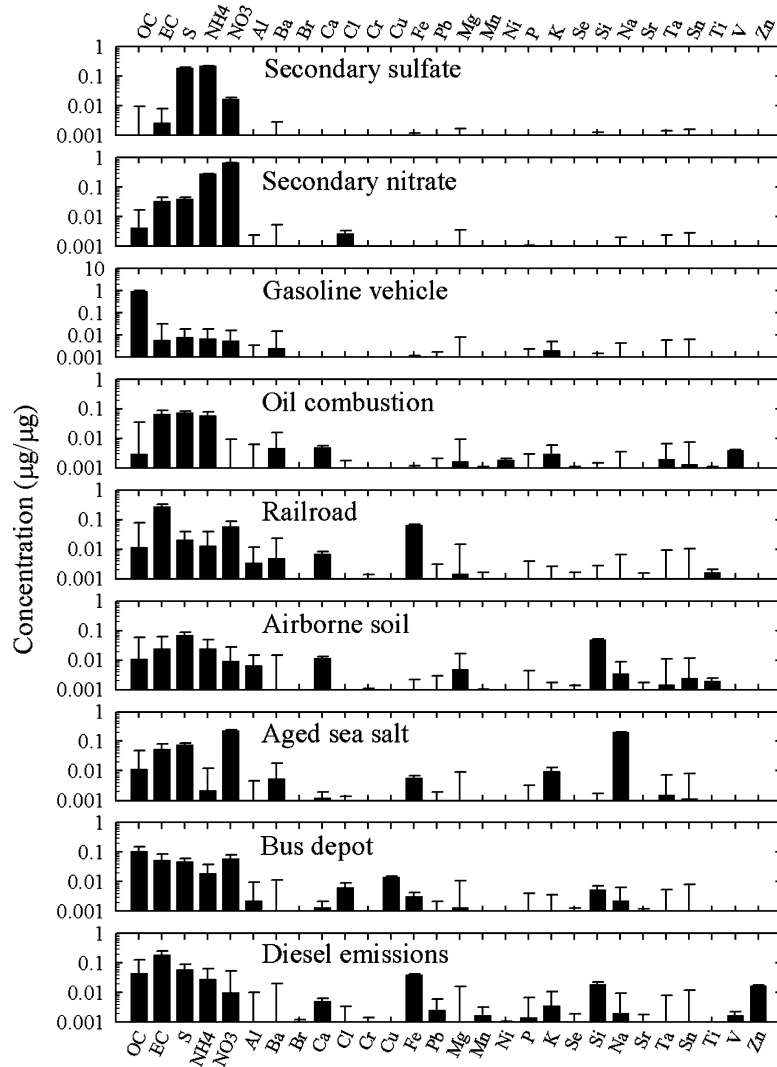


Figure 4. Source profiles deduced from $PM_{2.5}$ samples measured at the Wilmington site (prediction \pm standard deviation).

$42.0 \mu\text{g}/\text{m}^3$ (Camden), $45.8 \mu\text{g}/\text{m}^3$ (Wilmington) and $51.7 \mu\text{g}/\text{m}^3$ (Dover) on June 26, 2003. The air mass back trajectories were calculated for the days with high impacts using the HYSPLIT model starting height of 500 m above sea level using the vertical mixing model. As shown in Figure 6, the elevated contributions at four monitoring sites were likely to be caused by the regional transport of secondary particles from midwestern coal-fired power plants in the Ohio River Valley (Poirot *et al.*, 2001).

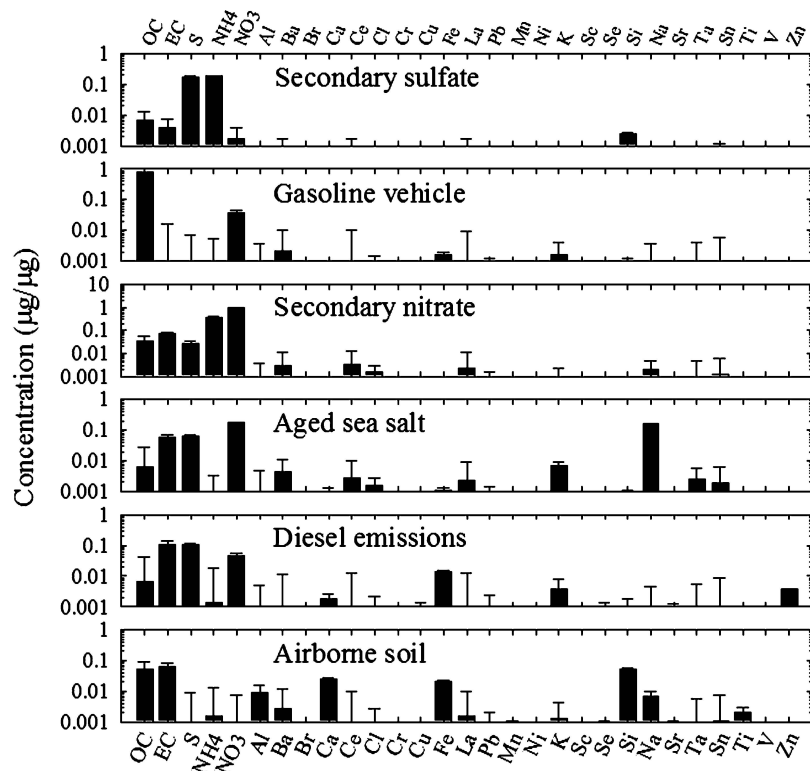


Figure 5. Source profiles deduced from PM_{2.5} samples measured at the Dover site (prediction \pm standard deviation).

The PSCF plots for the secondary sulfate are shown in Figure 7 in which PSCF values are displayed in terms of a color scale. These identified areas also include areas where the secondary sulfate were formed in addition to areas where the sources were located. Potential source areas and pathways that give rise to the high contribution to the four sites are located in Mississippi, Alabama, Georgia, Tennessee, western North Carolina, Florida, southern Kentucky, and the coast of the southern Mississippi. There remain some potential source areas in the Ohio River Valley and around St. Louis, MO. There are coal fired power plants along the Ohio River Valley, Tennessee Valley, Alabama, and Mississippi. Significant petrochemical industries are situated along the southern coast.

The prior PSCF analysis for IMPROVE data measured at a mid-Atlantic US site (i.e. Washington, DC) (Kim and Hopke, 2004a) showed that the high potential areas of the summer and winter-high secondary sulfate included Ohio River Valley, southern Kentucky, Tennessee, southern Louisiana, Mississippi, and Alabama. The potential source areas of secondary sulfate contributing to the four sites are similar to those of Washington, DC.

Secondary nitrate is represented by its high concentration of NO_3^- and NH_4^+ .

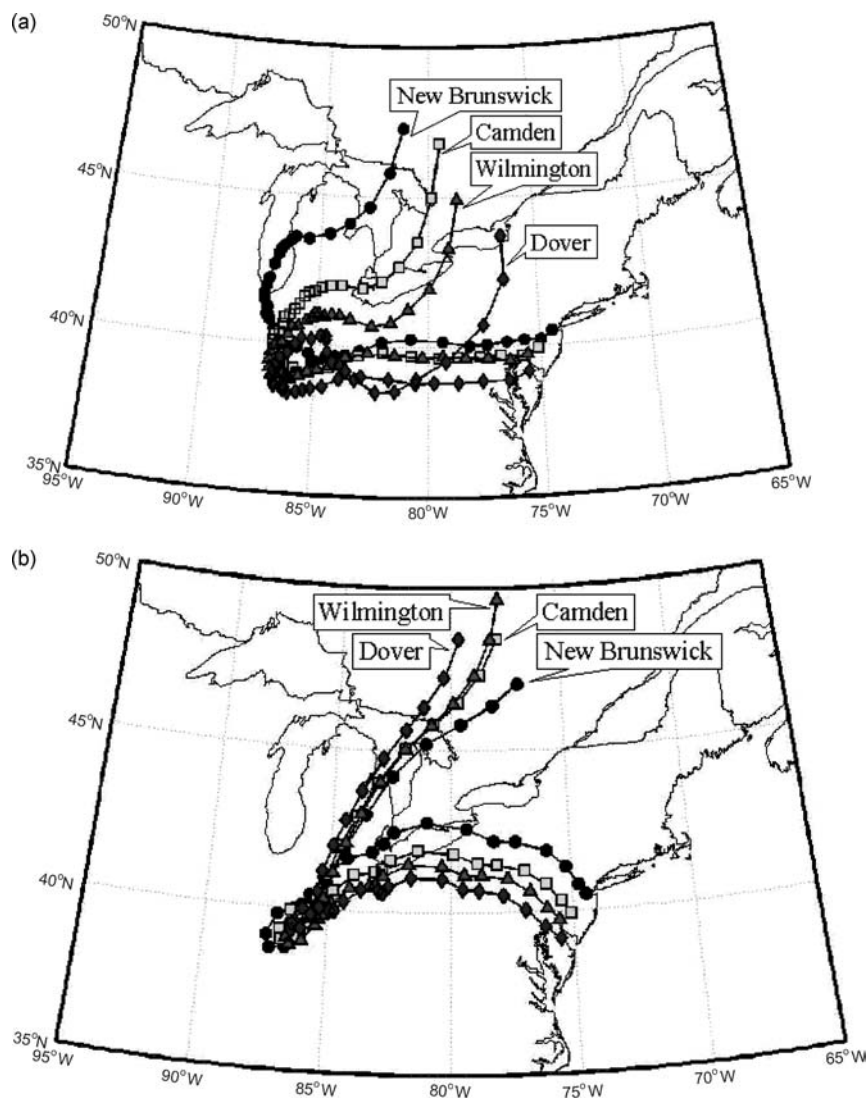


Figure 6. Backward trajectories arriving on (a) July 19, 2002 and (b) June 26, 2004 calculated from NOAA Air Resource Laboratory.

The average contributions of this source to the $PM_{2.5}$ mass concentrations were 9–18% at four monitoring sites. This source has seasonal variation with maxima in winter as shown in Figures 1, 4, 7 and 10 in the Appendix. These peaks in winter indicate that low temperature and high relative humidity help the formation of nitrate particles.

In Figure 8, the PSCF plots for the secondary nitrate contributions resolved at four monitoring sites are shown. Potential source areas and pathways that give

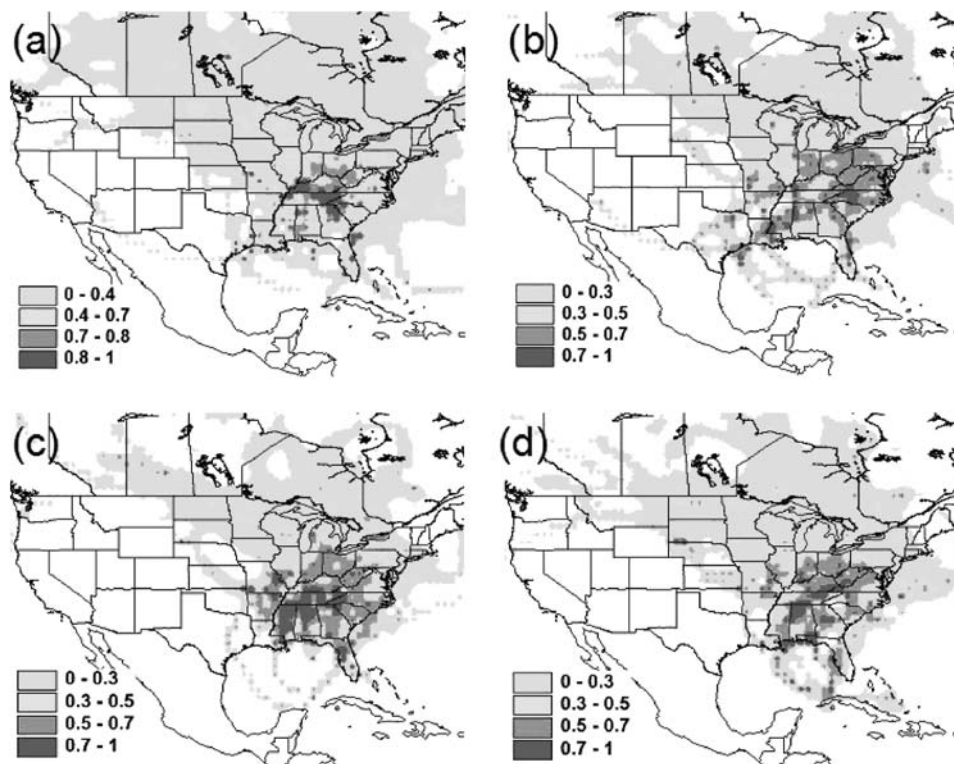


Figure 7. PSCF plots for the secondary sulfate identified at (a) New Brunswick, (b) Camden, (c) Wilmington, and (d) Dover.

rise to the high contribution to the four sites are located in Wisconsin, Missouri, Minnesota, South Dakota, Iowa, and Indiana. There is also potential source areas in Mississippi. The potential source areas of secondary nitrate contributing to the four min-Atlantic monitoring sites suggest that the secondary nitrate contributions may be the results of NH_3 out-gassed from the fertilizer use and animal husbandry in the US farm belt. Therefore, the PSCF plots point more to NH_3 source regions than to likely NO_3^- source areas.

It was possible to separate gasoline vehicle emissions from diesel emissions in all four STN data. Gasoline vehicle and diesel emissions are represented by high OC and EC, whose abundances differ between these sources (Watson *et al.*, 1994). Gasoline vehicles emissions have high concentration of the OC. In contrast, diesel emissions were tentatively identified on the basis of the high concentration of EC.

In Phoenix particle study, Lewis *et al.* (2003) found much higher diesel engine contributions on week days as compared to weekends. However, gasoline vehicle emissions had similar week day/weekend emissions. Previously, similar behavior has been observed in the eastern US (Kim and Hopke, 2004a,b). Thus, additional

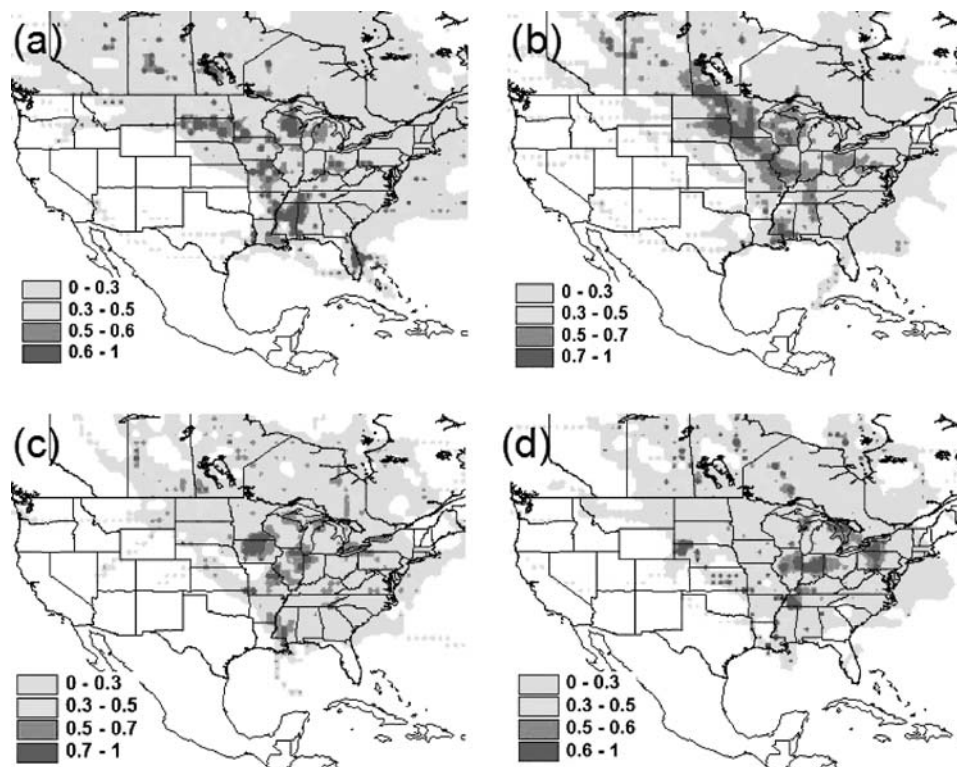


Figure 8. PSCF plots for the secondary nitrate identified at (a) New Brunswick, (b) Camden, (c) Wilmington, and (d) Dover.

support for the assignment of sources to gasoline vehicle and diesel emissions could be provided by observable differences in the contributions of these sources on week days and weekend days.

As shown in Figure 9, gasoline vehicle emissions do not show a strong week-day/weekend variations. In contrast, diesel emissions show high contributions on week days. These results support the hypothesis that diesel emissions from heavy-duty vehicles are more significant on week days when compared to the weekends. CPF values for gasoline and diesel emissions are plotted in polar coordinates in Figures 2, 5, 9 and 11 in the Appendix. For the diesel emissions identified in Dover, the high impact from west shown in the CPF plot and high S concentration in source profile indicate that diesel emissions identified in Dover site are likely to be a combination of emissions from the nearby railroad and on-road diesel vehicles. It appears that this combination of emissions explain the weak weekday/weekend variations of diesel emissions in the Dover site.

The local motor vehicle sources are identified by their high carbon concentrations and directionality from CPF analyses (Figure 10). Local motor vehicle source

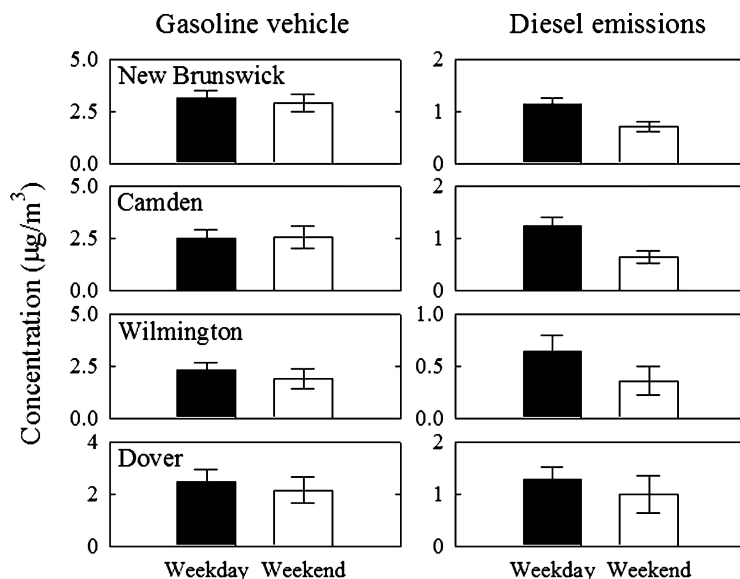


Figure 9. Weekday/weekend variations for gasoline vehicle and diesel emissions (mean \pm 95% confidence interval).

identified at New Brunswick appears to have contributions from northeast and southwest where the local roads are situated.

Another source with high concentration of OC and EC was identified in Wilmington. It has a high concentration of Cu that might come from the metallic brakes used on large vehicles and has commonly been seen in diesel profiles in other studies (Maykut *et al.*, 2003; Kim *et al.*, 2004; Kim and Hopke, 2004a,b). The site in Wilmington is near to a bus depot. This source may represent the emissions from the bus depot. The CPF plots of this source indicate impacts from bus depot located west of the site as shown in Figure 10. The bus depot profile does not include Zn and Ca that are often seen in the diesel emissions profiles. These elements appear in the separate diesel emissions profile and may be more strongly related to the on-road trucks moving at higher speed. The bus depot does not show strong weekday/weekend variations as shown in Figure 9 in the Appendix.

A third high-EC source was identified in Wilmington that has been tentatively assigned to be a combination of emissions from the nearby railroad and the Port of Wilmington. The main line AMTRAK tracks run parallel to the river to the south of the site, and the passenger terminal is situated southeast of the site. Although a large fraction of the trains are electric powered, there are a number of commuter and AMTRAK trains that use diesel engines. The profile contains a significant Fe concentration that was reported to be the major species emitted by electric trains in Zurich, Switzerland (Bukowiecki *et al.*, 2004). As shown in Figure 10, the CPF plot of this source shows the contributions from southwest and southeast where the

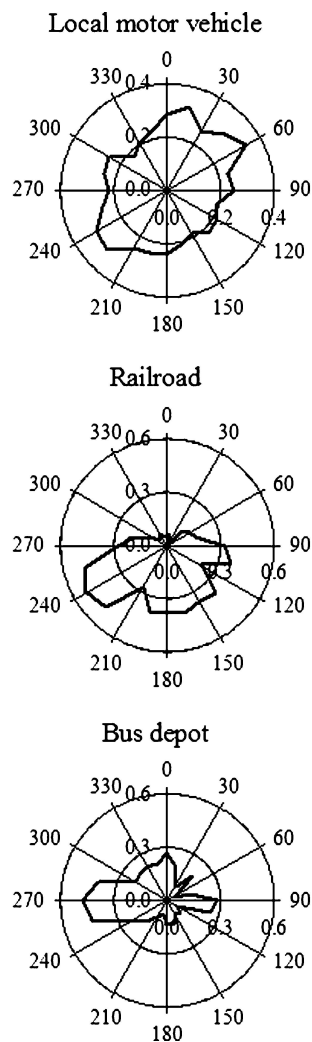


Figure 10. CPF plots for the highest 25% of the mass contributions for the local motor vehicle at New Brunswick, railroad and bus depot at Wilmington.

railroads and the Port of Wilmington are located. Railroad emission shows weekday-high variations. It appears that directional specificity helps resolve multiple point sources of carbonaceous particles in Wilmington.

The average contributions from gasoline vehicles to $PM_{2.5}$ mass concentration were 12–21% and diesel emissions were 3–7%. Local motor vehicle, bus depot, and railroad emissions contributed 5, 4, and 6% to $PM_{2.5}$ concentration, respectively.

These results need to be viewed in terms of recent study of Shah *et al.* (2004). They report that diesels operating at very slow speeds (creep) and in stop and go

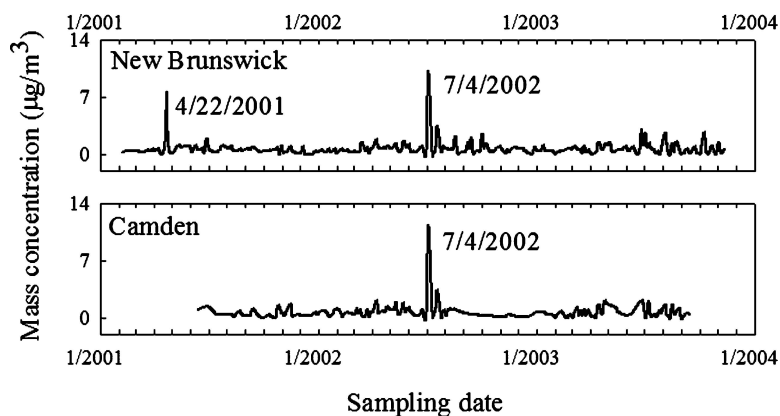


Figure 11. Time series plots of airborne soil contributions.

traffic produce OC/EC ratios that are like typical gasoline vehicle emissions. There is significantly more EC than OC in the emissions only under more continuous motion at higher speeds (transient and cruise). Thus, the diesel emission profile that is being extracted by PMF may represent only diesel vehicles moving at reasonable speed in fluid traffic conditions. Diesel vehicles in stop and go traffic are likely to be apportioned into the gasoline emission category.

Aged sea salt is characterized by its high concentration of Na, SO_4^{2-} and NO_3^- . The lack of chlorine in the profile is presumably caused by chloride displacement by acidic gases. Aged sea salt accounts for 5–10% of the $\text{PM}_{2.5}$ mass concentrations at four monitoring sites. This particle shows a winter-high seasonal pattern. Although the contaminated Na^+ collected between October 2001 and January 2002 were significantly down-weighted in PMF analyses, the source contributions of aged sea salt in this period were relatively high. Therefore, there is a possibility that this source contribution is still contaminated by some degree of artifact. As shown in Figures 2, 5, 8 and 11 in the Appendix, there are indications of higher contributions of this particle from the direction of Atlantic Ocean.

The airborne soil is represented by Si, Al, and Ca (Watson *et al.*, 2001a,b) contributing 5–7% to the $\text{PM}_{2.5}$ mass concentration at four monitoring sites. Crustal particles could be contributed by unpaved roads, construction sites, and wind-blown soil dust. The airborne soil shows seasonal variation with higher concentrations in the dry summer season. The elevated contribution on 4 July 2002 in Figure 11 was likely to be caused by a Sahara dust storm (Kim *et al.*, 2005). In contrast, the peak on 22 April 2001 was likely to be caused Asian dust storm that developed over Mongolia (NASA, 2001; Kim and Hopke, 2004b). Since the samples were not collected between July 1 and 7, 2002, the dust storm event was not identified in Wilmington and Dover studies. The elevated contribution of airborne soil on July 19, 2002 and June 26, 2003 at Wilmington shown in Figure 7 in the Appendix were

likely related to the regional transport from Midwest noted earlier (also shown in Figure 6).

Oil combustion is characterized by high concentrations of carbon fractions, V, and Ni reflecting residual oil combustion for the utilities and industries (Kim and Hopke, 2004a,b). This source contributed 5 and 8% to the $PM_{2.5}$ mass concentration in Camden and Wilmington, respectively. This source does not show strong week-day/weekend variations. The CPF plots of this source point to the southwest at Camden and the northeast and southeast at Wilmington (Figures 5 and 8 in the Appendix).

Previous backward trajectory analyses for the Vermont particle study indicated that major sources of oil combustion were located along northeastern urban corridor between Washington, DC and Boston, MA (Polissar *et al.*, 2001). There is a refinery in Delaware City which is south of the Wilmington site, and a large oil as well as coal-fired power plant is situated within a few km of Wilmington site to the south-southeast. There is a large oil-fired power plant in Salisbury, MD (southwest) and another moderate sized plant in Dover, DE (south). From the CPF plot, it appears that the Wilmington site is affected by those sources. Also, the higher contribution ($1.5 \mu\text{g}/\text{m}^3$) from oil combustion and the CPF analysis indicated that oil combustion particles at the Wilmington site were originated from oil-fired power plants and ship diesel emissions from the Port of Wilmington located southeast of the site.

An incinerator source is identified at New Brunswick by carbon, Zn, Pb, and Cl contributing 1% to the $PM_{2.5}$ mass concentration. This source has a seasonal trend with higher values in winter and does not show strong weekday/weekend variations.

4. Conclusions

PMF was applied to 24-hour averaged STN $PM_{2.5}$ speciation data collected from four urban sites located in mid-Atlantic US area between 2001 and 2003. Eight sources were extracted at New Brunswick, NJ, seven sources at Camden, NJ, nine sources at Wilmington, DE, and six sources at Dover, DE monitoring sites. Secondary sulfate and nitrate particles contributed 55–61% to the $PM_{2.5}$ mass concentration. The air mass backward trajectories shows that the high concentrations of secondary sulfate at four monitoring sites were likely to be caused by the regional transport of $PM_{2.5}$ from midwestern coal-fired power plants in the Ohio River Valley. The PSCF plots of secondary nitrate show NH_3 source regions originated from fertilizer use and animal husbandry. At four sites, the diesel emissions were separated from gasoline vehicle emissions, and their source profiles were similar. Also,

other combustion sources were separated: local motor vehicle, railroad, and bus depot emissions. PMF successfully identified aged sea salt, airborne soil, incinerator, and oil combustion. Intercontinental dust storm events were identified at New Brunswick and Camden. At Wilmington, the ship diesel emissions were identified with residual oil combustion.

Appendix

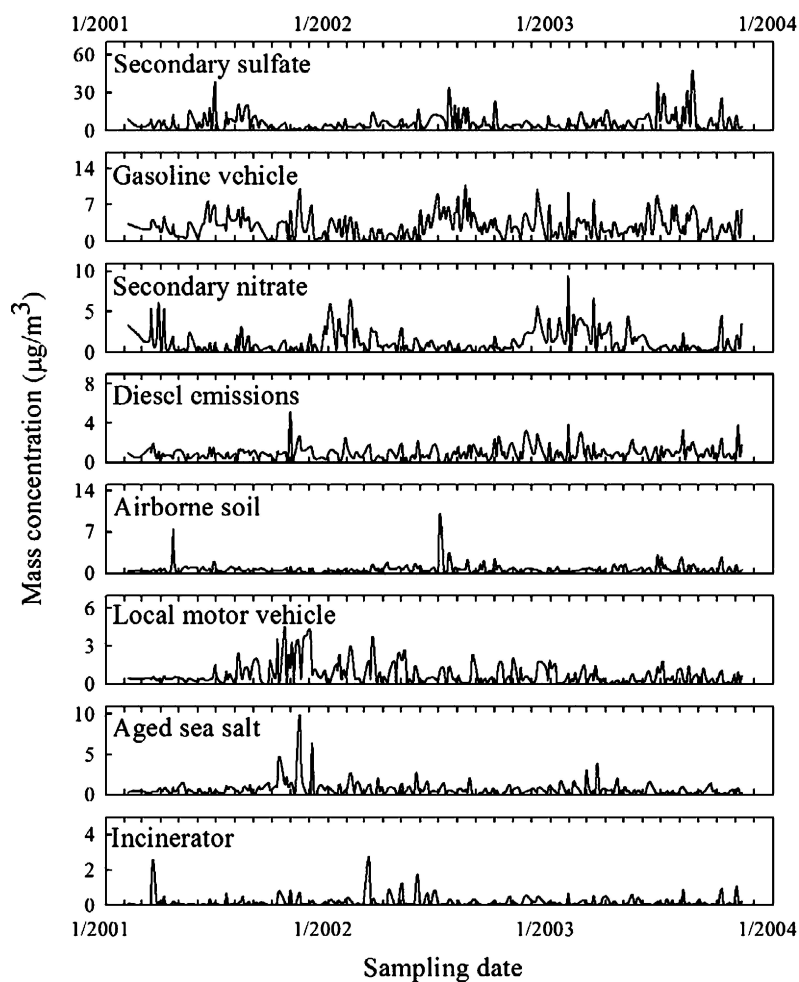


Figure A1. Time series plot of source contributions at the New Brunswick site.

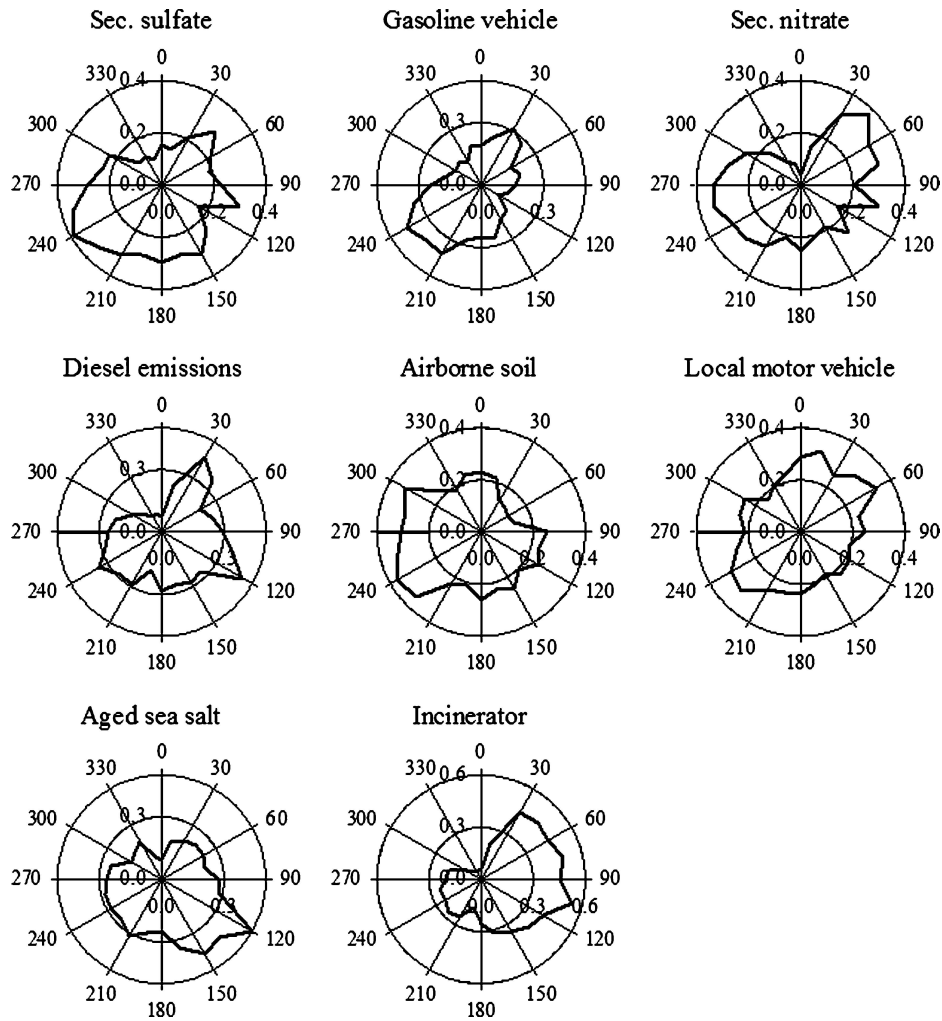


Figure A2. Conditional probability function plots for the highest 25% of the mass contribution at the New Brunswick site.

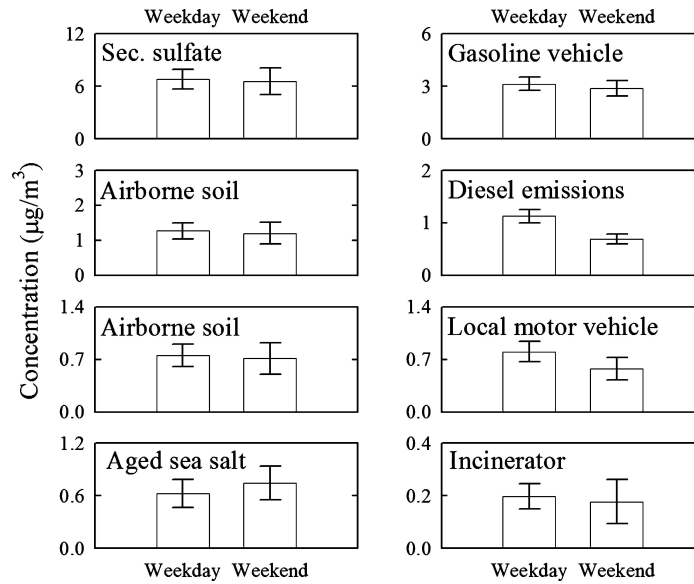


Figure A3. The comparisons of contributions between weekday and weekend at the New Brunswick site (mean \pm 95% confidence interval).

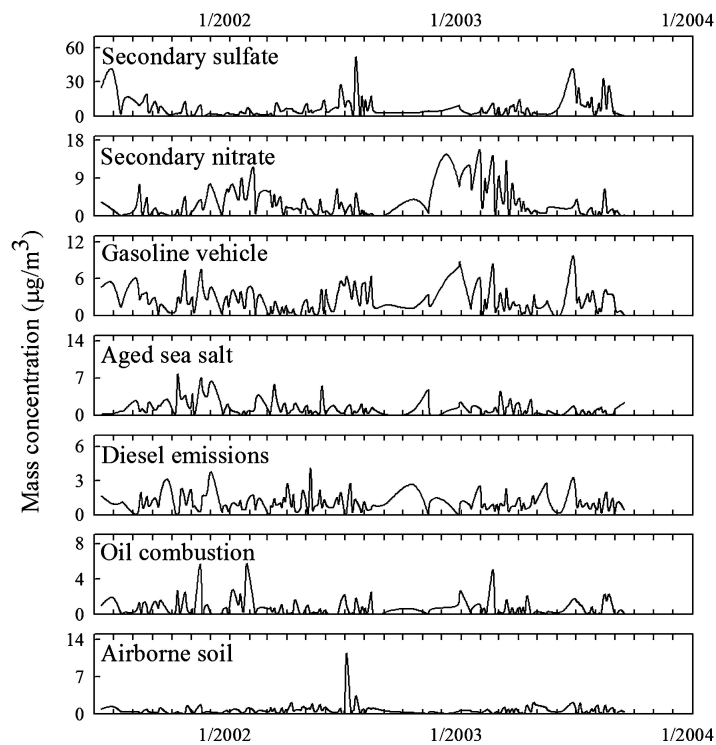


Figure A4. Time series plot of source contributions at the Camden site.

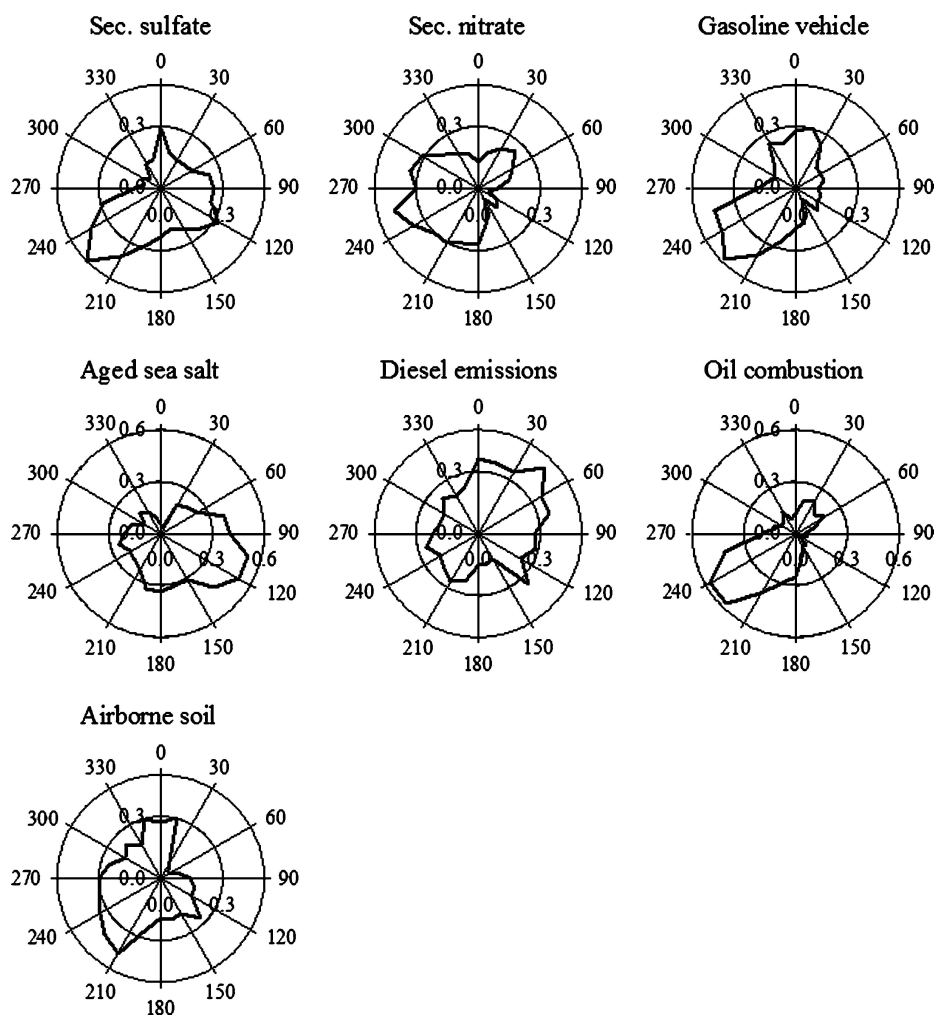


Figure A5. Conditional probability function plots for the highest 25% of the mass contribution at the Camden site.

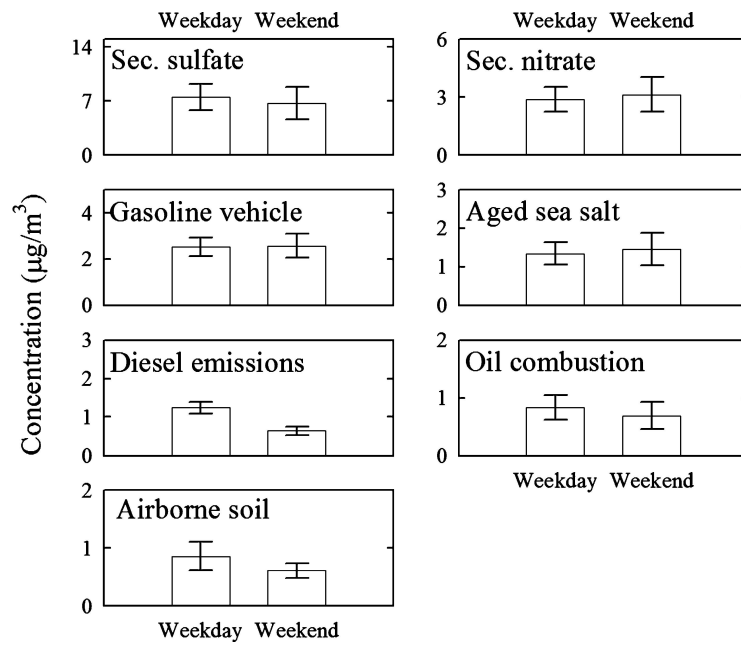


Figure A6. The comparisons of contributions between weekday and weekend at the Camden site (mean \pm 95% confidence interval).

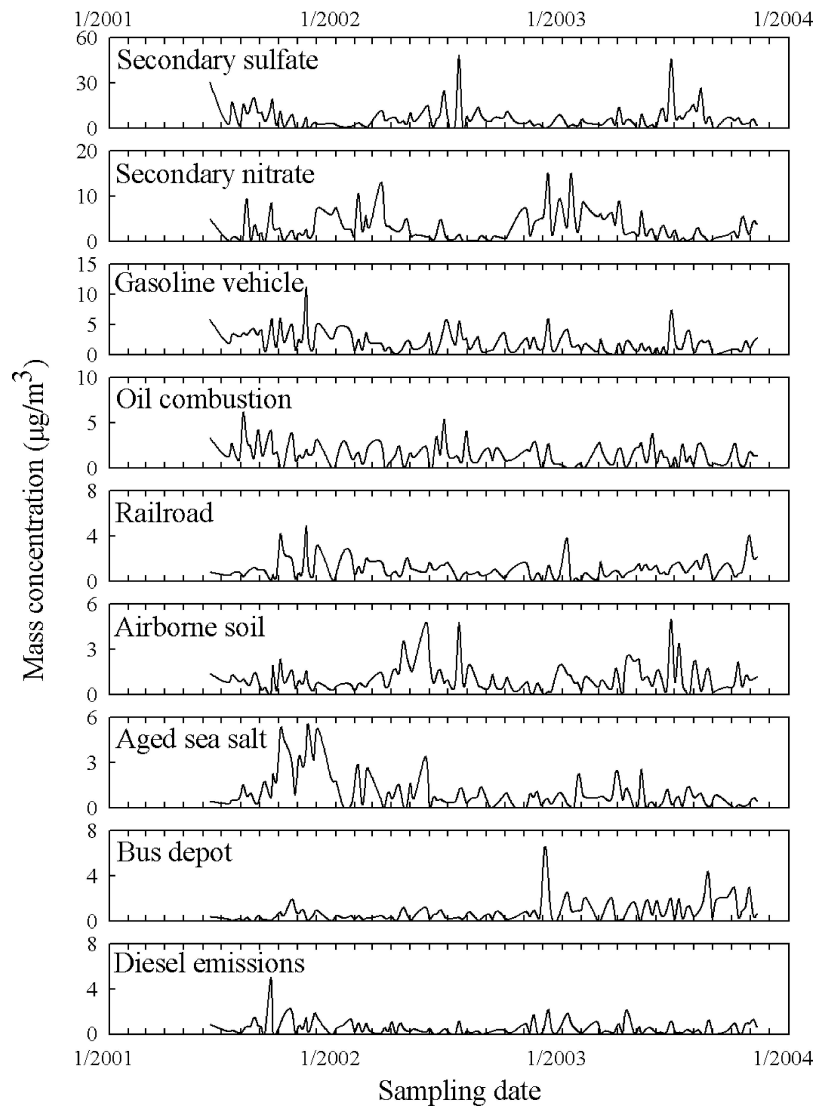


Figure A7. Time series plot of source contributions at the Wilmington site.

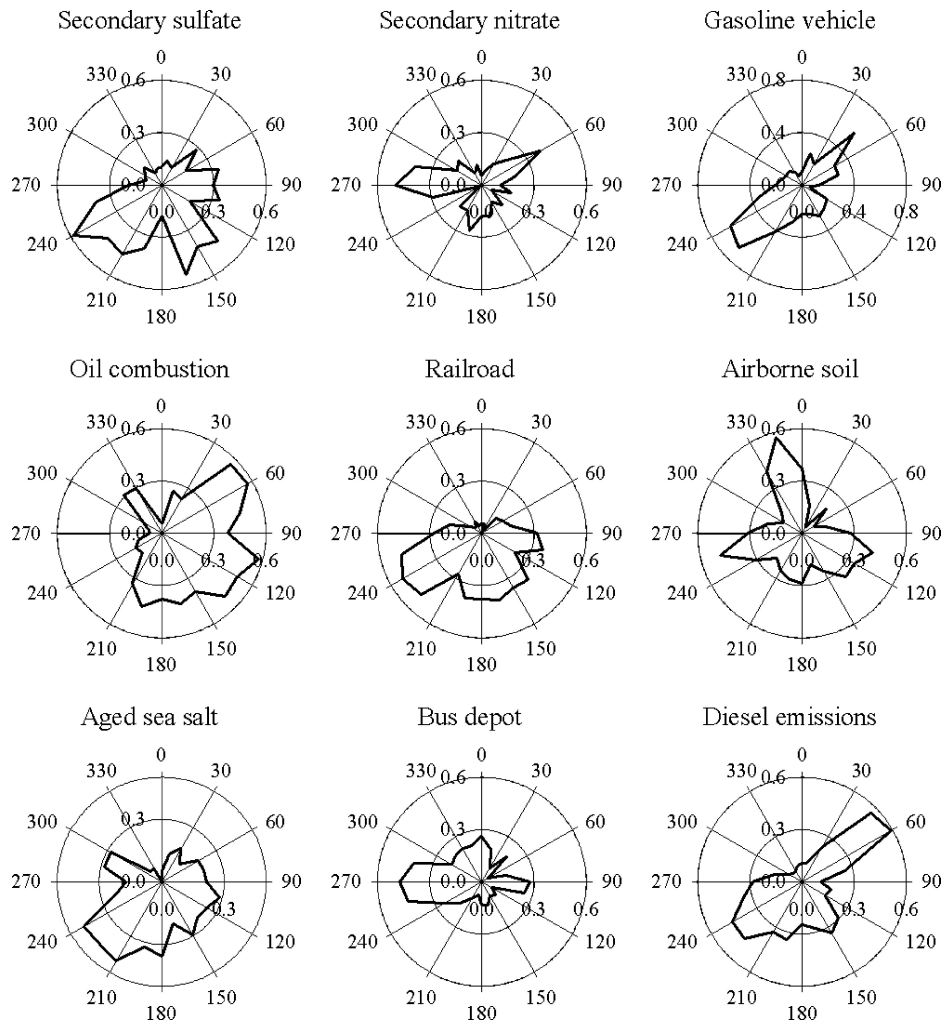


Figure A8. Conditional probability function plots for the highest 25% of the mass contribution at the Wilmington site.

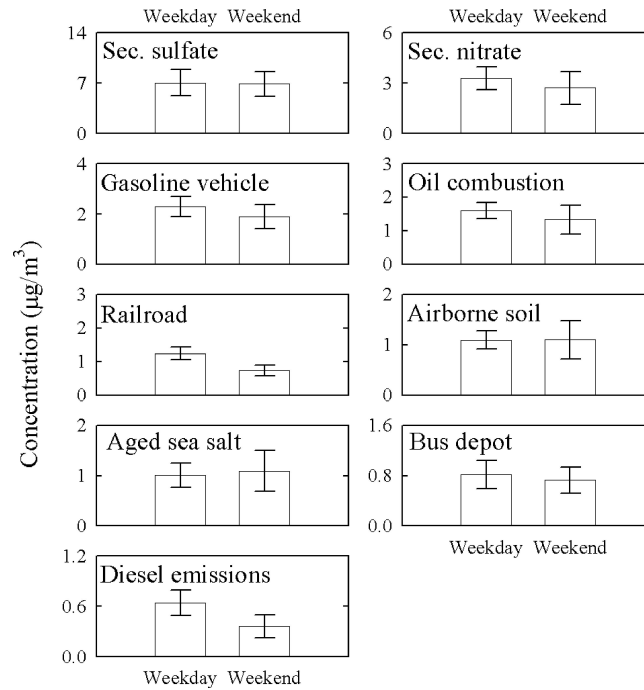


Figure A9. The comparisons of contributions between weekday and weekend at the Wilmington site (mean \pm 95% confidence interval).

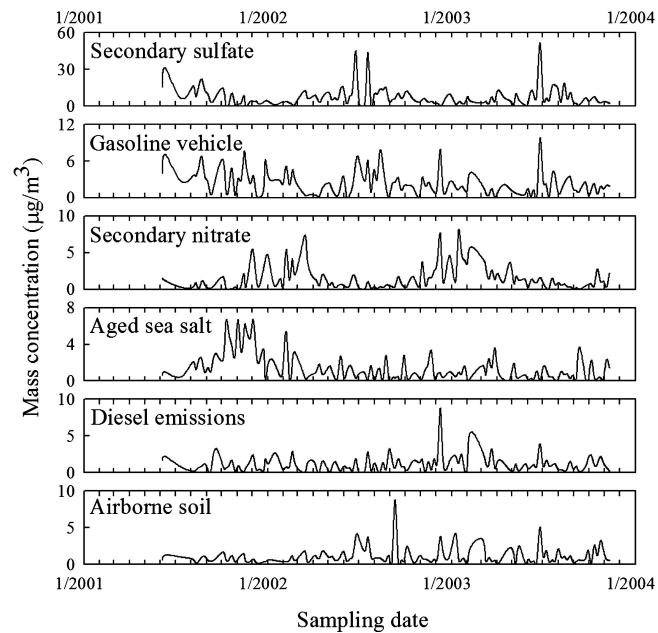


Figure A10. Time series plot of source contributions at the Dover site.

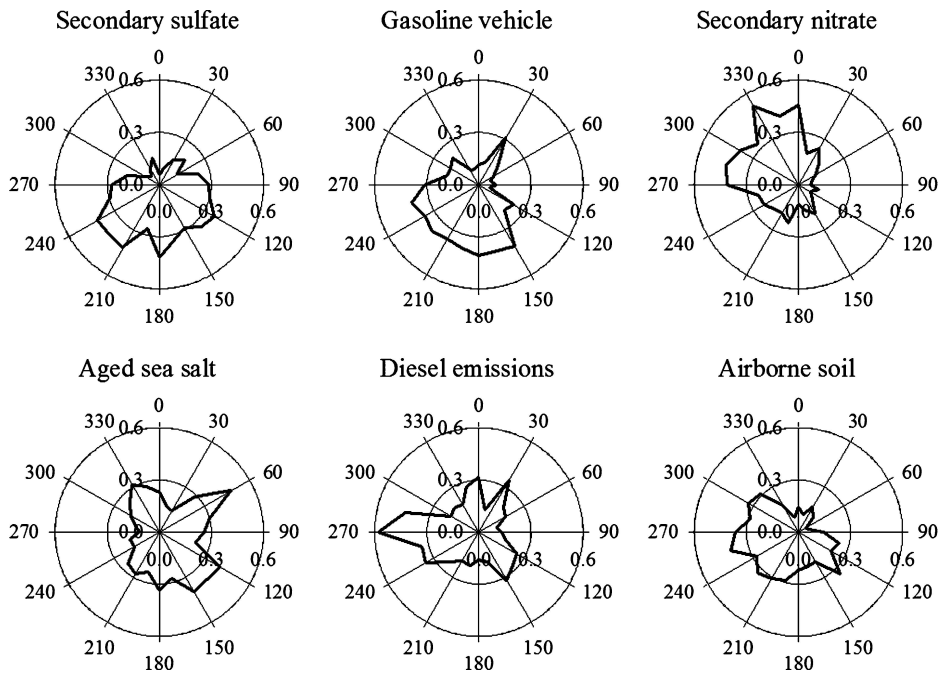


Figure A11. Conditional probability function plots for the highest 25% of the mass contribution at the Dover site.

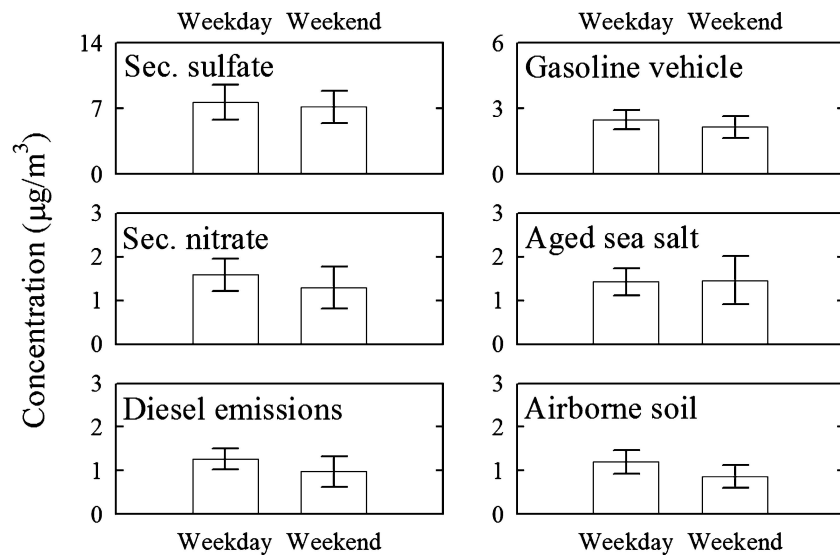


Figure A12. The comparisons of contributions between weekday and weekend at the Dover site (mean $\pm 95\%$ confidence interval).

Acknowledgments

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